

imum of one bottle of precipitation was collected for each event. This type of sample selectivity could bias any results obtained (6), making them unrepresentative of the precipitation as a whole.

The major result of the study of Frohlinger and Kane is that the total acid concentration of precipitation is much higher than the free acid concentration. However, the two possible sources of error discussed above either decrease the free acid concentration or increase the total acid concentration and thus these errors might be responsible for many of the differences found.

THOMAS J. MURPHY

Department of Chemistry,  
DePaul University,  
Chicago, Illinois 60614

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8 September 1975

Frohlinger and Kane (1) have reported acid-base titration figures for precipitation samples from a suburban site in Pennsylvania, and they have drawn some conclusions that are not fully substantiated by the data presented. Data from the European Air Chemistry Network (2), as well as from measurements in connection with the OECD Programme (3), indicate that the main chemical species in precipitation are  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$ . The precipitation acidity (free  $\text{H}^+$  at  $\text{pH} \approx 5$ ) is generally determined by the difference

$$[\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] - [\text{NH}_4^+]$$

If the titration procedure described by Frohlinger and Kane is used, some  $\text{NH}_4^+$  ions ( $\text{p}K_a = 9.25$  at  $25^\circ\text{C}$ , where  $\text{p}K_a$  is the negative logarithm of the dissociation constant) and dissolved  $\text{CO}_2$  will be titrated as weak acids. In order to un-

Table 1. Precipitation chemistry data from Birkenes, Norway, April to June 1973 (48 samples).

Ion	Weighted mean concentration	Weighted standard deviation from the mean
$\text{H}^+$	$68 \times 10^{-6}M$	$39 \times 10^{-6}M$
$\text{NH}_4^+$	$47 \times 10^{-6}M$	$34 \times 10^{-6}M$
$\text{NO}_3^-$	$31 \times 10^{-6}M$	$24 \times 10^{-6}M$
$\text{SO}_4^{2-}$	$44 \times 10^{-6}M$	$28 \times 10^{-6}M$

derstand the significance of the results of Frohlinger and Kane, it is necessary to know the concentrations of  $\text{NH}_4^+$  and the precautions taken to remove  $\text{CO}_2$  from the precipitation samples.

A program of chemical analysis for precipitation samples should include specific methods for determining the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and other components. It should also be realized that  $(\text{NH}_4)_2\text{SO}_4$  may act as a strong acid in a natural ecosystem. Our experience (3) is that the proportion of  $\text{NH}_4^+$  to  $\text{SO}_4^{2-}$  increases in air masses with continental origin. In contrast to Frohlinger and Kane's reference to Granat's results (2), we find a very high correlation between  $\text{SO}_4^{2-}$  and free  $\text{H}^+$  at Norwegian sites (correlation coefficient  $r = .8$  to  $.9$ ). Typical concentrations of major components are shown in Table 1. Obviously, the good correlation is due to the high acidity. Sites with higher  $\text{NH}_4^+$  concentrations will give poor correlation.

Weak organic acids are probably also present in precipitation samples. We feel, however, that more direct evidence is required to prove their occurrence in significant amounts. The chemical composition must also be known if the ecological effect is to be considered.

JAN SCHAUG  
AARNE SEMB

Norwegian Institute for Air  
Research, P.O. Box 15,  
2007 Kjeller, Norway

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7 October 1975

I object strongly to the conclusions of Frohlinger and Kane (1). Their data, with which I have no quarrel, indicate that Pennsylvania rainfall can contain as much as  $43 \times 10^{-5}$  mmole/ml of "weak acids," while the "free  $[\text{H}^+]$ " is usually less than  $8 \times 10^{-5}$  mmole/ml. This finding, they claim, "discredits the assumption that strong acids account for the presently observed  $\text{pH}$  value." The fact is that weak acids exert no control over the  $\text{pH}$  of a solution which has a  $\text{pH}$  much smaller than the  $\text{p}K_a$  (the negative logarithm of the equilibrium constant) of the acid; that is, once the weak acid is totally in the protonated form (HA), a stronger acid can lower the  $\text{pH}$  just as it would if no weak acid were present.

It may indeed be that the dissolution of anions of weak acids ( $\text{A}^-$ ) might raise the  $\text{pH}$  of a mineral acid solution by remov-

ing some of the free  $\text{H}^+$ ; this dissolution could account for the lack of the correlation between the free  $\text{H}^+$  and anions such as  $\text{SO}_4^{2-}$  in precipitation. One might, in fact, expect to find a fair amount of such weak acids and their anions in an atmosphere where substantial quantities of coal are burned. Since the  $\text{p}K_a$  of the most common carboxylic acids is in the range of 4 to 5, it is even possible that there are some unprotonated anions present. Their degree of protonation, however, and therefore the  $\text{pH}$ , can easily be altered by the addition of a stronger acid, such as  $\text{H}_2\text{SO}_4$ . For this reason I must argue that the presence of large quantities of weak acid in rainfall is not inconsistent with the idea that the species lowering the  $\text{pH}$  is  $\text{H}_2\text{SO}_4$  or some other strong acid.

BARRY J. HUEBERT

Department of Chemistry, Colorado  
College, Colorado Springs 80903

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2 September 1975

Frohlinger and Kane (1) have reported data they claim supports the hypothesis that acidic precipitation is a solution of weak acids. There is no evidence for this hypothesis from European precipitation samples, in which the measured  $\text{pH}$  is in good agreement with the predicted acidity based on the concentrations of major ions (2). Furthermore, the experimental data offered by Frohlinger and Kane do not provide evidence for the weak acid hypothesis.

The titrations described by Frohlinger

Table 1. Chemistry and titration data for precipitation collected in Oslo, Norway. Means and standard deviations of quadruplicate determinations are expressed as micromoles per liter.

Component	Episode 1, 2 October 1975	Episode 2, 4-5 October 1975
Free acid, $[\text{H}^+]$	$57 \pm 4$ ( $\text{pH}$ 4.25)	$18 \pm 2$ ( $\text{pH}$ 4.75)
$[\text{NH}_4^+]$	$42 \pm 3$	$6 \pm 4$
$[\text{H}_2\text{CO}_3]$	12	12
"Total acid" calculated, $[\text{HA}]$ , that is, $[\text{H}^+] + [\text{NH}_4^+] + 2[\text{H}_2\text{CO}_3]$	$123 \pm 7$	$48 \pm 6$
"Total acid" titrated, $[\text{HA}]$	With $\text{N}_2$ , $109 \pm 8$ Without $\text{N}_2$ , $135 \pm 4$	With $\text{N}_2$ , $45 \pm 15$ Without $\text{N}_2$ , $80 \pm 24$
$[\text{SO}_4^{2-}]$	$47 \pm 3$	$15 \pm 4$
$[\text{NO}_3^-]$	$29 \pm 2$	$3 \pm 1$
"Total acid" due to titration procedure (%)	20	45

# Science

## Acid Precipitation: Strong and Weak Acids

JAN SCHAUG and AARNE SEMB

*Science* **194** (4265), 646.

DOI: 10.1126/science.194.4265.646

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